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MELTING CONDITIONS FOR QUARTZ GLASS OF HIGH PURITY AND STRUCTURAL PERFECTION

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New operations and new methods of performing the known operations of purification of quartz grit are proposed on the basis of an analysis of the quartz formation conditions in different deposits, the structure and physical-chemical properties of the quartz, and known technologies for producing quartz grit. The optical characteristics of quartz glasses made from natural and synthetic raw materials by different vacuum-melting methods are compared.

Key words: quartz, grit, purification, quartz glass, vacuum melting, certification of glass.

One method of certifying quartz raw material, quartz enrichment technologies, and melting methods is to fuse certified ingots of quartz glasses and analyze their optical macro-, micro- and other characteristics. The vacuum-compression method of fusing ingots of single-component and doped quartz glasses ranging in mass from tens of grams to one kilogram is predominately used at the Institute of Mineralogy of the Urals Branch of the Russian Academy of Sciences. Melting is done in a quartz crucible placed in a molybdenum crucible or an ampoule following the technology for melting KS-4V glass but using natural quartz raw material. The melting methods permit melting glass ingots similar to KI and KI-UK glasses [1]. Their visible and infrared range optical characteristics are identical to those of KS-4V glass but differ by lower light transmission at wavelengths 190 – 350 nm.

The technological possibilities for melting quartz glass and the availability of different types of quartz raw materials with known purity and impurity composition make it possible to perform experiments to determine the effect of different impurities and conditions of melting on the optical characteristics of glasses.

The particulars of the optical transmission spectrum of glass are a certification criterion for glass quality.

Taking into account the particulars of natural quartz from different deposits, paragenetic aggregates and mineral bodies and the physical-chemical and mechanical properties of quartz individuals and analyzing the conditions for their possible technogenic contamination, changes in a number of methods used to perform individual operations and entirely new operations in the enrichment technology for quartz raw material were proposed. The enrichment efficiency was checked by vacuum-compression melting of certified ingots and studying their optical characteristics and macro-structural perfection.

Effect of the Comminution Method for Crushed Stone on Quartz Grit Quality

The initial operation in the commercial technology for obtaining preliminary-enrichment quartz grit (KPO) is thermal comminution of crushed stone.

However, it must be kept in mind that the ontogeny of vein quartz and the phylogeny of its parageneses are always accompanied by co-crystallization from fluid or water solutions of the hydroxides of silicon, aluminum, iron, manganese, magnesium, alkali and other elements.

Existing data show that the specific surface area of hydrogoethite is 570 m^2/g while that of ferromanganese nodules (FMN) reaches 300 m^2/g, i.e., their sorption capacity can be high [2, 3]. It has been established that marine ferromanganese nodules possess high sorption capacity with respect to an entire series of metals [4]. It is known that when ferromanganese nodules are heated to 1000 °C their specific surface area decreases to 0.2 m^2/g because the hydroxides are converted into water-free modifications [5]. This should result in an inversely proportional increase of the specific concentration of adsorbed impurities. The high mechanical and chemical stability together with impurities of newly formed compounds preserved in them can decrease the efficiency of deep purification of grit.

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A direct experiment was performed to check these suppositions. Crushed material was prepared from a chunk of granulated quartz and divided into two parts of equal mass. One half was comminuted by heating to 1000°C and the other half without heating. A KPO (preliminary enrichment quartz) quartz concentrate was prepared from both types of grit, and the same technological scheme was used to prepare KGO (deep enrichment quartz) grit. Quartz glass ingots were made from concentrates with grain fractions from 0.1 to 0.4 mm by vacuum-compression melting. A study of the optical characteristics and macro-structural perfection of the glasses showed that the ingot made from grit prepared by comminution without heating the crushed material was of superior quality.

Dependence of Grit Purity on Grain Size

Model and direct experiments established that when granulated quartz is comminuted the fine grit fraction is enriched with impurity mineral inclusions [6]. This is due to strength and brittleness differences between the mineral inclusions and quartz. Smelting glass ingots from granulated-quartz grit with particle size from 0.2 to 0.4 mm and from 0.1 to 0.2 mm, which were obtained by sorting the initial grit with particle size 0.1 – 0.4 mm, showed that with respect to the optical and structural properties the glass obtained from 0.2 – 0.4 mm grit is superior to that obtained from the fine fraction.

The relation is reversed for first-crystallized milky-white quartz, because quartz contains few mineral but many gas-liquid (GLI) inclusions. For this reason, mineral inclusions do not become concentrated in fine grit fraction, while GLI are well revealed mechanically in the fine fraction and their contents can be removed by leaching.

Equipment Contamination of Grit during Comminution of Crushed Material

Considerable contamination of quartz grit by technogenic impurities occurs during mechanical comminution of crushed material. The level of technogenic contamination is illustrated by an experiment performed with milky-white quartz from the Zhelannoe deposit. A sample of this quartz was divided into parts. One part was comminuted manually with a quartz-glass pestle in a mortar made of the same material. The other part was comminuted with a DM 200 disk mill, manufactured by the Retsch Company, with steel disks. When the grit produced by manual abrasion was subjected to magnetic separation there were virtually no ferromagnetic inclusions. For the grit obtained by abrasion in a disk mill such inclusions comprised 0.17% of the initial mass of the grit. Both quartz grits were enriched once to the maximum values using the same technology. Two glass ingots were smelted from the 0.1 – 0.2 mm fraction of the concentrates obtained. Certification of the glass samples showed substantial reduction of glass quality as a result of technogenic contamination of the grit during mechanical comminution of the quartz.

Microwave Decrepitation of GLI in Quartz Grit

One operation in the purification of quartz grit is thermal decrepitation of GLI in grains at temperature 200 – 1200°C. The process is energy and materials intensive and too inefficient because the quartz itself is heated, which increases plasticity and decreases brittleness. The higher the heating temperature, the more plastic the material is and the more difficult it is to break down a mineral individual.

In [7] the compositions of GLI in minerals were studied using decrepitation by exposure to microwave radiation. In this case a mineral grain remains practically cold and its brittleness does not decrease, which makes more efficient decrepitation of GLI possible. It was of interest to study the possibility of using this method of decrepitation in grit enrichment technology.

Comparative experiments studying the efficiency of thermal decrepitation (TD) and microwave decrepitation (MD) were performed [8]. Grit of granulated quartz from the Berkutinskaya vein (Kyshtymskoe deposit), quartz from the Tolstikha gold vein (Southern Urals) and milky-white quartz from the Zhelannoe deposit (Polar Urals) were subjected to decrepitation. The number of grains containing GLI was different in grits of different fractions and in grits from different deposits. Grit from the Tolstikha vein was white and contained the largest number of GLI. Grit from the Zhelannoe deposit was grayish-white, semitransparent and contained fewer GLI. Even fewer GLI were present in the predominately transparent grit from the Berkutinskaya vein. Grits of all fractions from the deposits were divided into two parts each part comprising 50 g to within 10 mg. One part of the grit was heated in an alundum crucible at 600°C for 1 h in a laboratory furnace. The other part was heated at maximum power in a plastic vessel in a LG microwave furnace for 5 min. The temperature of the grits was 60 ± 10°C after microwave heating; the grits were not cooled. The grit heated at 600°C was poured onto a metal pan and cooled to room temperature. The quartz grains with GLI definitely fractured during decrepitation and, in consequence, were comminuted. After decrepitation all forms of grit were sieved in precisely the same time 5 min through a sieve with cells of size equal to the lower limit of the grit fractions. The sieved grits were weighed on electronic scales to within 10 mg and the MD and TD efficiency was evaluated by comparing the sieved mass. The results obtained for the MD and TD efficiency for quartz grit from different deposits and with different particle sizes were presented in Table 1.

The experimental results presented in the Table 1 show that microwave heating increases decrepitation efficiency for individual grits to 55%. The MD efficiency is proportional to the GLI content in grit and inversely proportional to the grit grain size. Microwave decrepitation shortens the process time considerably and decreases energy consumption and ex-

TABLE 1. Results of Microwave and Thermal Decrepitation of Quartz Grit Made with Raw Material from Different Deposits

Fraction, mm	Deposit								
	Berkut			Zhelannoe			Tolstikha		
	% sieved material		Efficiency, %	% sieved material		Efficiency, %	% sieved material		Efficiency, %
	TD	MD		TD	MD		TD	MD	
< 0.315	17.3	20.2	116	5.4	6.9	126	5.3	8.1	155
< 0.2	16.5	18.0	109	5.2	6.0	115	3.4	4.6	134
< 0.1	11.4	11.9	104	4.8	5.2	107	–	–	–

TABLE 2. Results of Qualitative Chemical Analysis of Agglomerates

Sample test No.	Si	Na	K	Mg	Ca	Ba	Al	P	Ti	Cr	Mn	Fe	O	Total
1	22.68	1.14	1.08	1.84	–	–	2.36	–	1.94	1.13	–	24.65	38.64	95.45
2	27.09	3.95	1.72	2.41	–	–	8.24	–	1.37	–	0.27	9.71	45.28	100.05
3	34.13	2.05	0.64	1.72	–	–	2.30	–	0.90	0.27	–	10.05	46.52	98.58
4	35.10	2.81	1.00	2.11	–	–	4.00	–	0.79	–	–	4.30	47.88	98.00
5	23.96	4.15	2.94	0.43	–	–	17.97	–	1.06	–	–	3.83	47.42	101.75
6	32.14	3.12	1.40	0.25	4.92	0.77	4.85	0.39	–	–	–	1.63	45.49	94.95
7	23.07	5.86	0.0	–	1.95	–	9.34	–	–	–	–	–	37.42	77.65
8	33.81	7.05	0.39	–	1.74	–	11.76	–	–	–	–	–	52.21	106.96
9	31.50	8.42	–	–	0.63	–	10.50	–	–	–	–	–	48.40	99.50

penditures on the heat-resistant technological ware required for decrepitation. Microwave decrepitation gives more complete exposure of GLI, which should increase the purity of quartz grit.

Agglomeration Method of Removing Mineral Inclusions from Quartz Grit

The removal of naturally occurring mineral inclusions from quartz grit is an extremely difficult problem.

It is known that most mineral inclusions in quartz grit and impurities in the bulk, on the surface of quartz grains and in the boundaries between grains melt at temperatures below 1350°C [9]. When grit is heated it can melt, forming characteristic melts and impurity-quartz glass phases on the surface of quartz grit [10]. Melts of inclusions and glass phase promote smelting (sticking) of neighboring sand grains, forming agglomerates that can be easily removed by sieving after cooling.

The method proposed above was tested on two brands of quartz concentrates with the fractions 0.2 – 0.4 and 0.1 – 0.2 mm — KPO (pre-enrichment quartz) and KGO (deep-enrichment quartz), made using quartz obtained from a number of deposits. The number and sizes of the agglomerates and their color range are distinguished according to fractions and types of quartz. A qualitative analysis of the chemical composition of a number of agglomerates distinguished by color and size was performed with a JXCAS-733 microprobe analyzer (Table 2).

The first six results in Table 2 pertain to agglomerates formed by sintering a quartz grain with colored minerals, whose color varies from black to yellow. Dark particles (results 1 – 3) are agglomerates with a high content of iron and titanium. The next four results pertain to light-colored agglomerates. It is evident that the colored agglomerates contain iron, titanium, calcium and sometimes chromium. The colorless agglomerates (results 7 – 10) do not contain, first and foremost, iron and titanium and often they do not contain calcium. Apparently, the colored agglomerates are formed by micaceous minerals and iron and titanium oxides, while the colorless agglomerates are formed by feldspar minerals.

The experiments showed that a number of impurities can be removed by temperature agglomeration. The optical transmission spectra and shadow photography of the macrostructure of glass ingots made from commercially enriched grit and the same grits additionally purified by agglomeration show that agglomeration purification greatly improves the qualitative characteristics of quartz grit.

Melting Method Effect on the Optical Properties of Quartz Glass

The optical transmission spectra of quartz glasses smelted from a single batch of high-purity concentrate prepared at the Kyshtym Mining-Enrichment Combine from the

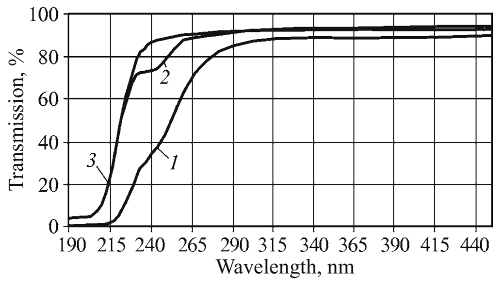

Fig. 1. Optical transmission spectra (1 – 3) of glasses made from the same grit of naturally occurring raw material: *1*) vacuum-compression melting in a crucible — V-C M; *2*) vacuum-compression melting of heated raw material in an ampoule in oxygen in a melting chamber — V-C M A ox.; *3*) vacuum-compression melting in ampoule by heating raw material using active gases in a melting chamber V-C M act.gas.

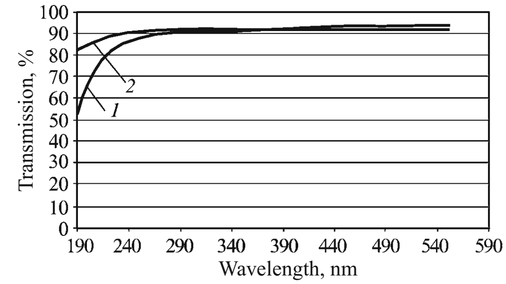

Fig. 2. Optical transmission spectra of quartz glasses smelted from: *1*) synthetic silicon dioxide by vacuum-compression melting sint. Sil. V-C M; *2*) synthetic silicon dioxide by vacuum-compression melting in an ampoule by calcination of raw material by active gases in a melting chamber sint.sil. V-C M A act.gas.

raw material in vein No. 175 are presented in Fig. 1. The No. 1 glass was made by vacuum-compression melting in a quartz crucible with a tungsten resistance heater. The No. 2 glass was made in a quartz ampoule in the same furnace with grit pre-heated in oxygen.

The No. 3 glass was also smelted in the same furnace using KI-UK technology, i.e., in a quartz ampoule with remelted grit processed in a medium consisting of active gases, hydrogen, oxygen and chlorine. The curves of the transmission spectra of glasses made by the vacuum-compression methods from the same raw material but with different melting conditions differ considerably. The curve *1* shows that optical transmission begins to decrease at 300 nm. This behavior in this transmission range is typical for quartz glasses made from highly purified class SSQ (KGO) concentrate or IOTA quartz grit from the UNIMIN Company (USA). Most researchers are of the opinion that the distinct inflection of the curve in the wavelength range 240 – 245 nm is due to the concentration of intrinsic structural defects of the glass (oxygen interstitial atoms and vacancies) as well as the presence of structural impurities Fe, Al, Ge and others.

The curve *2* shows that a shift of the conditions of melting in the oxidation direction (pre-melting heating in oxygen) improves the optical characteristics of quartz glass. Transmission begins to drop sharply at wavelength 260 nm, and the typical inflection of the transmission curve at 240 – 245 nm, characteristic of quartz glasses made in a deep vacuum, shifts into the range 230 – 240 nm, which could be due to the concentration of structural impurities.

It is unlikely that heating in oxygen substantially decreases the concentration of impurity Fe, Al and Ge atoms. The observed effect is probably due to a decrease of the concentration of intrinsic defects of the oxygen network in the glass.

The curve *3* of the optical transmission spectrum of glass made from raw material which has undergone pre-melting processing in an active-gas medium (hydrogen, oxygen, chlorine) shows substantial improvement of glass quality. Optical transmission starts to decrease at wavelength 250 nm, while the characteristic inflection in the spectrum at wavelengths 230 – 240 and 240 – 245 nm is absent. This is probably due to the fact that the purity of the quartz grit increases during high-temperature processing by active gases because of the formation of volatile hydrides and chlorides. Calcination of the grit in an oxygen medium decreases the concentration of oxygen defects, improving the optical characteristics of the glass in the UV wavelength range.

To check the effect of the concentration of oxygen defects on the spectral characteristics of quartz glass made from synthetic silicon dioxide (SSD), whose impurity content is known to be low, two glass ingots were smelted. One ingot was obtained by the KS-4V technology and the other by vacuum-compression melting, just as KI glass. The optical transmission spectra of quartz glasses smelted from SSD raw material by the KS-4V technology for melting glass and by the KI glass technology are presented in Fig. 2. The spectral curves show that vacuum melting of ultrapure synthetic quartz raw material degrades its optical characteristics in the UV range. This could be due to a high concentration of oxygen defects in the structure of the glass.

REFERENCES

1. I. I. Cheremisin, V. S. Rudenko, A. Z. Bazurin, et al., "Method for obtaining optical quality quartz glass from artificial and vein quartz," in: *Abstracts of Reports at the 7th Scientific-Technical Conference on Quartz Glass* [in Russian], St. Petersburg (1991), pp. 49 – 50.
2. O. N. Karaseva, S. A. Pivovarov, L. Z. Lakshtanov, and L. I. Ivanova, "Investigation of the changes of the specific surface area of iron [III] hydroxide during recrystallization," in: *15th Russian Conference on Experimental Mineralogy: Conference Proceedings (Syktyvkar, June 22 – 24, 2005)* [in Russian], Institute of Geology, Komi Science Center, Urals Branch of the Russian Academy of Sciences, Geoprint, Syktykvar (2005), p. 370.
3. Yu. A. Nefedov, L. I. Anelok, S. N. Kilesso, and E. V. Kryukov, "Physical-chemical and metallurgical properties of marine concretions," *Geologiya Poleznye Iskopaemye Mirovogo Okeana*, No. 1, 51 – 55 (2005).

4. I. G. Lugovskaya, “Use of complex mineralogical methods to study the technological properties of ferromanganese marine ores,” in: *15th Russian Conference on Experimental Mineralogy: Conference Proceedings (Syktyvkar, June 22 – 24, 2005)* [in Russian], Institute of Geology, Komi Science Center, Urals Branch of the Russian Academy of Sciences, Geoprint, Syktyvkar (2005), pp. 481 – 483.
5. S. I. Anufrieva, V. N. Sokolova, and D. O. Ozhogin, “Experimental study of sorption materials based on marine ferromanganese incrustations,” in: *15th Russian Conference on Experimental Mineralogy: Conference Proceedings (Syktyvkar, June 22 – 24, 2005)* [in Russian], Geoprint, Syktykvar (2005), pp. 447 – 448.
6. R. Sh. Nasyrov, “Technological concentration of mineral impurities in the fine fraction of quartz powder during comminution,” *Steklo i Keramika*, No. 5, 37 – 39 (2009); R. Sh. Nasyrov, “Technological concentration of mineral admixtures in the fine fraction of quartz powder during milling,” *Glass Ceram.*, **66**(5 – 6), 192 – 193 (2009).
7. B. Z. Belashev and L. V. Kuleshevich, “Decrepitation of gas-liquid inclusions in quartz from different genetic types of gold-ore manifestations in Karelia,” *Geology and Minerals of Karelia* [in Russian], KarNTs RAN, Petrozavodsk (2005), Issue 8, pp. 89 – 94.
8. R. Sh. Nasyrov, “Microwave decrepitation of gas-liquid inclusions in quartz grains,” *Obogashchenie Rud*, No. 2, 26 – 27 (2009).
9. N. A. Smolyaninov, *Practical Manual on Mineralogy* [in Russian], Nedra, Moscow (1972).
10. N. A. Toropov, V. P. Barzakovskii, V. V. Lapin and N. N. Kurtseva, *Handbook of Phase Diagrams for Synthetic Systems* [in Russian], Nauka, Leningrad (1969).